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# Kinetic study of hydrogen sulfide absorption in aqueous chlorine solution

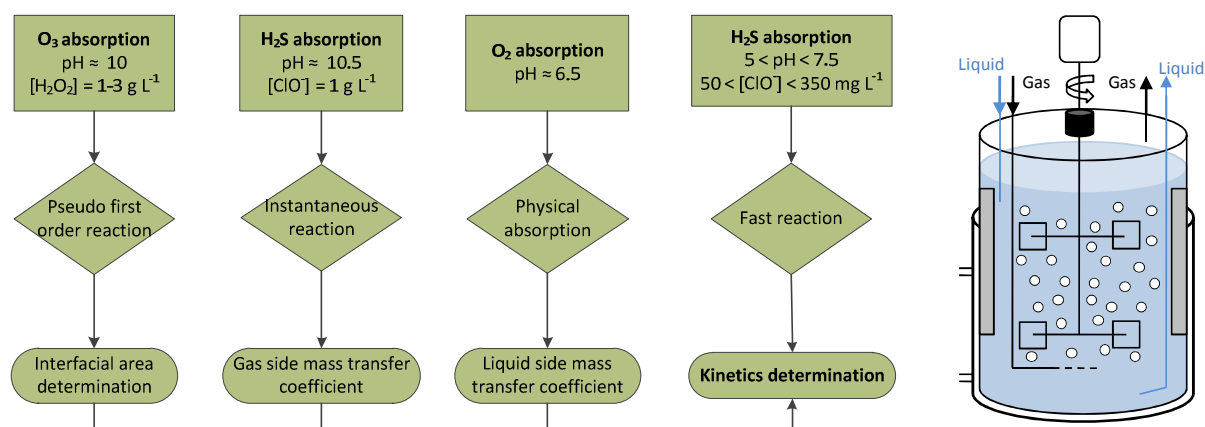
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## Graphical abstract



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## *Abstract*

Hydrogen sulfide ( $\text{H}_2\text{S}$ ) is currently removed from gaseous effluents by chemical scrubbing using water. Chlorine is a top-grade oxidant, reacting with  $\text{H}_2\text{S}$  with a fast kinetic rate and enhancing its mass transfer rate. To design, optimize and scale-up scrubbers, knowledge of the reaction kinetics and mechanism is requested. This study investigates the  $\text{H}_2\text{S}$  oxidation rate by reactive absorption in a mechanically agitated gas-liquid reactor. Mass transfer (gas and liquid sides mass transfer coefficients) and hydrodynamic (interfacial area) performances of the gas-liquid reactor were measured using appropriated physical or chemical absorption methods. The accuracy of these parameters was checked by modeling the  $\text{H}_2\text{S}$  absorption in water without oxidant. A sensitivity analysis confirmed the robustness of the model. Finally, reactive absorption of  $\text{H}_2\text{S}$  in chlorine solution for acidic or circumneutral pH allowed to investigate the kinetics of reaction. The overall oxidation mechanism could be described assuming that  $\text{H}_2\text{S}$  is oxidized irreversibly by both hypochlorite anion  $\text{ClO}^-$  ( $k = 6.75 \cdot 10^6 \text{ L mol}^{-1} \text{ s}^{-1}$ ) and hypochlorous acid  $\text{ClOH}$  ( $k = 1.62 \cdot 10^5 \text{ L mol}^{-1} \text{ s}^{-1}$ ).

## *Keywords*

Hydrogen sulfide, chlorine, kinetics, mass transfer, absorption, scrubber

## *Highlights*

- Kinetics of  $\text{H}_2\text{S}$  oxidation by chlorine is investigated using a well agitated reactor
- Mass transfer and hydrodynamics performances of the reactor are determined
- Sensitivity analysis is performed to assess the robustness of the modeling
- $\text{H}_2\text{S}$  reacts irreversibly with hypochlorous acid and hypochlorite anion
- Kinetic constants are determined

# 1 Introduction

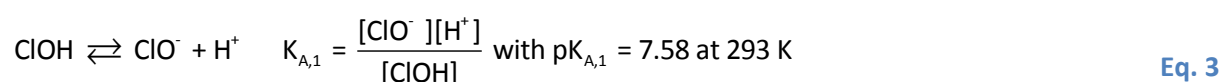
Hydrogen sulfide (H<sub>2</sub>S) is a major toxic compound involved in odor emissions of many industries such as waste water treatment, pulp industry, etc. (Gostelow et al., 2001; Kangas et al., 1984; Rappert and Müller, 2005). Proving high and reliable efficiency, chemical wet scrubbing is the most widely used process to prevent H<sub>2</sub>S emissions (Busca and Chiara, 2003; Smet and Langenhove, 1998; Smet et al., 1998). This technique involves H<sub>2</sub>S mass transfer in an aqueous phase using a gas-liquid contactor. Since H<sub>2</sub>S is poorly soluble in water, to increase its removal efficiency, aqueous oxidant solutions at basic pH are often used (Biard et al., 2009; Bonnin, 1991; Chen et al., 2001; Kerc and Olmez, 2010; Le Sauze et al., 1991). Other processes are currently used to remove H<sub>2</sub>S : biofiltration, absorption in alkanolamine solutions, absorption using the Claus process or catalysts to recover the elemental sulfur, etc. (Busca and Chiara, 2003; Kohl and Nielsen, 1997).

Due to a strong reactivity with H<sub>2</sub>S, chlorine is a top-grade oxidant for this application and is currently used, especially in waste water treatment plants, in rendering and composting facilities, etc. The process is operated semi-continuously (Biard et al., 2010). The scrubbing liquid is stored in a tank located at the bottom of the scrubber and is recirculated. pH and chlorine concentration are regulated. This scrubbing liquid is just drained when the salt accumulation due to H<sub>2</sub>S oxidation into sulfate anions becomes too high.

Chlorine speciation in water is rather complex. Depending on the pH, the ionic strength and the chloride concentration, chlorine can be present in water mainly as aqueous chlorine Cl<sub>2</sub>, hypochlorous acid ClOH and hypochlorite ions ClO<sup>-</sup> (Deborde and Von Gunten, 2008):

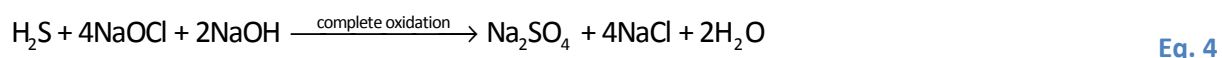


$$K_{\text{Cl}_2} = \frac{[\text{ClOH}][\text{H}^+][\text{Cl}^-]}{[\text{Cl}_2]} = 3.8 \times 10^{-4} \text{ mol}^2 \text{ L}^{-2} \text{ at } 293 \text{ K and a negligible ionic strength} \quad \text{Eq. 2}$$



Cl<sub>2</sub> exists only at acidic pH (pH < 5-6) and its coexistence domain increases with the total chloride concentration. Some additional species such as Cl<sub>3</sub><sup>-</sup>, Cl<sub>2</sub>O can be observed. However, at a low chloride concentration, they can be neglected (Deborde and Von Gunten, 2008). With a higher oxidation potential, ClOH currently reacts faster than ClO<sup>-</sup>. These observations emphasize that oxidation kinetics with chlorine are pH dependant.

An excess of chlorine (at least 4 mol of chlorine for 1 mol of H<sub>2</sub>S) can mineralize H<sub>2</sub>S (oxidation number = -2) in sulfate ion (oxidation number = +6) according to the following global mechanism at alkaline pH:



The first by-product formed after H<sub>2</sub>S oxidation is elemental sulfur which can be further oxidized in sulfite SO<sub>3</sub><sup>2-</sup> and sulfate SO<sub>4</sub><sup>2-</sup> (Choppin and Faulkenberry, 1937). In the whole process, oxidation of elemental sulfur into sulfite is considered as the rate limiting step, especially at pH close to the neutrality where colloidal sulfur accumulation can be observed in chemical scrubbing processes (Biard et al., 2009; Bonnin, 1991).

H<sub>2</sub>S is a weak diacid in equilibrium with its conjugated base, the hydrosulfide anion HS<sup>-</sup> (pK<sub>A,2</sub> = 7.07 at 293°K (Roustan, 2003)). The sulfide anion S<sup>2-</sup> is present only at very basic pH and can be neglected (pK<sub>A,3</sub> = 13.94 at 293°K) at pH used in chemical scrubbing (pH ≤ 11-12). During H<sub>2</sub>S chemical scrubbing in chlorine solutions, both H<sub>2</sub>S dissociation in HS<sup>-</sup> and oxidation decrease the H<sub>2</sub>S bulk concentration, which maintains a maximal and constant mass transfer driving force. Moreover, since the kinetics of these reactions are really fast, mass transfer enhancement is currently observed, which leads to a large removal efficiency (Biard et al., 2010). Indeed, mass transfer enhancement due to these reactions enhances the absorption rate by decreasing the mass transfer resistance in the liquid film (Roustan, 2003). By this way, the whole resistance could be located in the gas phase. Mass transfer enhancement calculation is rather complicated and depends on several parameters: nature (reversible, irreversible) and number of reactions involved, reaction(s) kinetics, reaction(s) stoichiometry, concentrations and diffusion coefficients (van Swaaij and Versteeg, 1992).

Within the current operating conditions, which insure an excess of chlorine (several hundred mg L<sup>-1</sup> are usually set), H<sub>2</sub>S and HS<sup>-</sup> cannot be measured in the liquid bulk since they are quickly oxidized in the liquid film at the vicinity of the gas-liquid interface. From wet scrubbing experiments in packed column, Bonnin (1991) determined an apparent kinetic constant between H<sub>2</sub>S and ClOH of 1.8×10<sup>8</sup> L mol<sup>-1</sup> s<sup>-1</sup> for pH ranging from 9 to 11 at 293 K. However, this determination was based on wrong assumptions (Biard et al., 2010). Therefore, the kinetic rate of H<sub>2</sub>S oxidation by chlorine is poorly known whereas it would enable better gas-liquid contactor scale-up, design and optimization.

To answer to this issue, the purpose of this study is to determine the H<sub>2</sub>S oxidation kinetics at 293 K with ClOH and ClO<sup>-</sup>. Only a few techniques like stopped flow or competitive methods or reactive absorption can be used to determine high kinetic constants (Beltrán, 2004). In this particular case, reactive absorption seems to be appropriated (Vaidya and Kenig, 2007b). This technique has been

successfully applied in the past to determine kinetic constants in the fields of ozonation, chlorine hydrolysis, flue desulfurization or CO<sub>2</sub> capture in amine solutions (Aieta and Roberts, 1986; Beltrán, 2004; Ebrahimi et al., 2003; Jia et al., 2010; Jing et al., 2012; Kucka et al., 2002; Sema et al., 2012; Sotelo et al., 1991; Vaidya and Kenig, 2007a, 2009).

During H<sub>2</sub>S absorption, H<sub>2</sub>S removal efficiency is governed by the mass transfer rate which depends on the hydrodynamic and mass transfer performances of the reactor, gas and liquid flow patterns and H<sub>2</sub>S oxidation kinetic rate. If all these parameters are controlled, the kinetics can be investigated. To simplify the liquid flow pattern and to insure a homogeneous liquid phase, a gas-liquid contactor agitated by a Rushton turbine has been selected. First of all, the mass transfer and hydrodynamic parameters of the laboratory tank must be determined in controlled conditions (gas and liquid flow rates, pressure, rotation speed). These parameters are determined by physical absorption of oxygen and by chemical absorption of ozone and H<sub>2</sub>S in specific mass transfer regimes. Then, the kinetic constant at 293 K can be deduced during H<sub>2</sub>S absorption in chlorine solutions set at various concentrations and pH. Chlorine concentration must be optimized to find a compromise between a too low kinetic rate on the one hand and a too large kinetic rate on the other hand to enable an accurate enhancement factor determination. pH will be in the range 5-7.5 to assess the influence of the chlorine speciation and to limit the potential HS<sup>-</sup> formation. The next section reviews the mass transfer theory which is required for the gas-liquid contactor characterization and the kinetic constant determination.

## 2 Mass transfer modeling

Gas-liquid mass transfer can be described according to various theories. Usually, the double film theory (explicative scheme in the supplementary material) is applied in steady state (Whitman, 1923). The molar flux transferred of any species A ( $dJ$  in  $\text{mol m}^{-2} \text{s}^{-1}$ ) per square meter of gas-liquid area can be written (Perry and Green, 1997):

$$dJ = Ek_L (C_A^* - C_A) = K_L (C_A^{Eq} - C_A) \quad \text{Eq. 5}$$

$E$  is the so-called enhancement factor (no unit) which is the ratio of the absorption rate with and without the reaction for an identical difference  $C_A^* - C_A$ . Other definitions of the enhancement factor can be found in the literature. However, this one remains the most encountered.  $C_A$ ,  $C_A^*$ ,  $C_A^{Eq}$  are the solute concentration respectively in the bulk ( $\text{mol m}^{-3}$ ), at the gas-liquid interface (superscript \*) and in equilibrium (superscript Eq) with the gas phase concentration  $C_A^G$  deduced from the Henry's law:

$$C_A^{Eq} = \frac{p_A}{H_A} = \frac{R \times T \times C_A^G}{H_A} \quad \text{Eq. 6}$$

$p_A$  is the partial pressure (Pa),  $H_A$  the Henry's law constant ( $\text{Pa m}^3 \text{mol}^{-1}$ ).  $k_L$  and  $K_L$  (Eq. 4) are respectively the local and overall liquid side mass transfer coefficients ( $\text{m s}^{-1}$ ) which are linked together through the following relation:

$$\frac{1}{K_L} = \frac{1}{Ek_L} + \frac{RT}{H_A k_G} \quad \text{Eq. 7}$$

$k_G$  is the local gas side mass transfer coefficient.  $k_L$  and  $k_G$  order of magnitude are respectively  $0.5\text{-}5 \cdot 10^{-4} \text{ m s}^{-1}$  and  $0.5\text{-}5 \cdot 10^{-2} \text{ m s}^{-1}$  for most gas-liquid contactors (Roustan, 2003). The liquid-phase relative mass transfer resistance  $R_L$ , which represents the ratio of the resistance located in the liquid phase divided by the total resistance, is calculated by the following equation (Hoffmann et al., 2007; Rejl et al., 2009):

$$R_L = \left( 1 + \frac{RTEk_L}{H_A k_G} \right)^{-1} \text{ and } R_G = 1 - R_L \quad \text{Eq. 8}$$

In addition to the interface mass transfer and chemical kinetics, the performance of a gas-liquid contactor depends on the extent of mixing in both the phases (Joshi et al., 1982). Assuming that the liquid flow is perfectly mixed, *i.e.* complete back-mixing, the solute bulk concentration is uniform in the whole reactor which possesses an effective volume  $V$  (gas and liquid volumes sum). The extent of mixing for the gas phase depends on the impeller speed and the gas flow rate through the gas hold-

up (Lee and Pang Tsui, 1999). At a moderate impeller speed, the power input is not sufficient to disperse the gas in the part of the reactor located below the sparger. In this case, the extent of back-mixing is low and the flow can be considered as a plug flow. The role of the agitation is to break bubbles to maintain a high interfacial area. Assuming a plug flow for the gas and a perfectly mixed liquid, the absorption rate ( $N$  in  $\text{mol s}^{-1}$ ) can be calculated by the following equation:

$$N = K_L a^\circ V (C_A^{Eq} - C_A) = K_L a^\circ V \frac{(C_{A,i}^{Eq} - C_A) - (C_{A,o}^{Eq} - C_A)}{\ln \frac{C_{A,i}^{Eq} - C_A}{C_{A,o}^{Eq} - C_A}} \quad \text{Eq. 9}$$

Subscripts i and o refer to the reactor inlet and outlet.  $a^\circ$  is the gas-liquid interfacial area ( $\text{m}^2 \text{m}^{-3}$ ) relative to the effective volume  $V$ . The mass balance enables to write:

$$N = Q_G (C_{A,i}^G - C_{A,o}^G) \quad \text{Eq. 10}$$

$Q_G$  is the gas volume flow rates ( $\text{m}^3 \text{s}^{-1}$ ). From Eqs. 6-10:

$$\ln \frac{\frac{RTC_{A,i}^G}{H_A} - C_A}{\frac{RTC_{A,o}^G}{H_A} - C_A} = K_L a^\circ \frac{VRT}{H_A Q_G} = \frac{a^\circ}{\frac{1}{Ek_L} + \frac{RT}{H_A k_G}} \frac{VRT}{H_A Q_G} \quad \text{Eq. 11}$$

When the reaction rate is significantly larger than the mass transfer rate, the solute is entirely consumed in the liquid film and  $C_A$  tends toward 0. In the other cases,  $C_A$  depends on the liquid hold-up, liquid residence time and on the kinetic and mass transfer rates (Lee and Pang Tsui, 1999). Except for two limit cases (slow and instantaneous reactions in the liquid film),  $E$  depends on the reaction kinetics. Therefore, its determination in controlled and appropriated operating conditions could enable kinetics determination.  $k_L$  and  $k_G$  are mainly influenced by the properties and hydrodynamics of respectively the liquid and the gas phases. The interfacial area depends on the gas hold-up and bubbles size, which are determined by the flow field, the gas flow-rate, the power input and the gas dispersion characteristic of the impeller (RESI, 2013). Except the gas side mass transfer coefficient which has never been measured for a gas-liquid agitated tank, they can be estimated using semi-empirical correlations (Calderbank, 1958; Calderbank, 1959; Joshi et al., 1982; Lee and Pang Tsui, 1999). In this study, for a better accuracy, they will be determined prior to  $E$  measurements.



### 3 Material and methods

Different chemical systems were implemented to determine  $\alpha^\circ$  (ozone absorption in a solution of hydrogen peroxide),  $k_L$  (physical absorption of pure oxygen),  $k_G$  (chemical absorption of  $H_2S$  in highly concentrated chlorine alkaline solution) and  $E$  ( $H_2S$  chemical absorption in slightly acidic or neutral chlorine solution) (Table 1).  $H_2S$  absorption in pure water was also investigated to assess the accuracy of  $\alpha^\circ$ ,  $k_L$  and  $k_G$  determination. The parameters are deduced from the removal efficiency (Eq. 12) of each absorbed species:

$$Eff_A = \frac{C_{A,i}^G - C_{A,o}^G}{C_{A,i}^G} \quad \text{Eq. 12}$$

Table 1: Synthesis of the physical and chemical operating conditions applied.

	Parameter	Value	Experimental uncertainty
<b>Physical operating conditions</b>			
	Temperature $T$	293 K	$\pm 1$ K
	Effective volume $V$	1.65 L	$\pm 0.05$ L (3%)
	Impeller speed	250 rpm	
	Liquid flow rate $Q_L$	7-30 L h <sup>-1</sup>	3.0%
	Gas flow rate $Q_G$	400-750 NL h <sup>-1</sup>	3.1%
<b>Chemical operating conditions</b>			
<b><math>\alpha^\circ</math> measurement</b> O <sub>3</sub> absorption in H <sub>2</sub> O <sub>2</sub> solution	Inlet H <sub>2</sub> O <sub>2</sub> concentration	1173-2720 mg L <sup>-1</sup>	2.1%
	pH	9.9-10.15	$\pm 0.1$ unit
	Inlet O <sub>3</sub> concentration	35-60 g Nm <sup>-3</sup>	2%
<b><math>k_L</math> measurement</b> O <sub>2</sub> physical absorption	pH	6.5	$\pm 0.1$ unit
	Inlet O <sub>2</sub> concentration	Pure oxygen	
<b><math>k_G</math> measurement</b> H <sub>2</sub> S absorption in ClOH solution	pH	10.4-10.8	$\pm 0.1$ unit
	Inlet H <sub>2</sub> S concentration	110-135 mg Nm <sup>-3</sup>	10%
	Inlet chlorine concentration	1 g.L <sup>-1</sup>	2.1%
<b>Absorption of H<sub>2</sub>S in water</b>	pH	8-8.1	$\pm 0.1$ unit
	Inlet H <sub>2</sub> S concentration	50-65 mg Nm <sup>-3</sup>	10%
<b>Absorption of H<sub>2</sub>S in chlorine solution</b>	pH	5-7.5	$\pm 0.1$ unit
	Inlet H <sub>2</sub> S concentration	50-150 mg Nm <sup>-3</sup>	10%
	Inlet chlorine concentration	50-350 mg L <sup>-1</sup>	2.1%

### 3.1 Presentation of the experimental set-up

The laboratory-scale glass gas-liquid contactor (1 in Fig. 1) is a nominal 2 liters tank mechanically agitated by a Rushton turbine (impeller diameter of 4.5 cm and vessel diameter of 11.0 cm). The liquid phase is prepared in a 50 L Nalgene® storage tank (2) using demineralized water. Concentrated NaOH or H<sub>3</sub>PO<sub>4</sub> solutions are added to set the pH. Depending on the chemical system implemented, chlorine or hydrogen peroxide can be also added to set a given oxidant concentration. The reactor is fed and drained by an inlet (3) and an outlet centrifugal pumps (4). Flow rates are controlled by means of valves and measured by two flowmeters (3',4'). The contactor temperature is controlled at 20 ± 1 °C with an isothermal liquid circulating in the reactor jacket (5). The pH of the liquid and the temperature are measured on-line using a combined pH-probe (6). Fresh air is introduced using a gas pump (7). Then a gas flow of N<sub>2</sub>-H<sub>2</sub>S (8) is mixed with the pumped air thanks to a static mixer (10). These two flows are controlled by means of valves and measured by float-type flowmeters (7',8') (Sho Rate R6-15-C and R6-15-D) and dispersed in the reactor by a titanium sparger (11). Before starting the experiments, the gas-liquid contactor is by-passed to analyze the gas inlet at steady-state. For the interfacial area determination, the feed system is replaced by an ozone generator fed with oxygen. In this case, the ozone flow rate is controlled by a flowmeter in Teflon®. During the experiments, a fraction of the gas is by-passed to analyze the outlet at steady-state (12). Before being released in the atmosphere, residual O<sub>3</sub> and H<sub>2</sub>S in the gas phase were quenched using respectively an ozone destructor and by bubbling in a concentrated basic chlorine solution (13). The gas pressure is measured twice, at the flowmeter outlet to correct the flow rate and in the reactor headspace, using manometers.

Each float-type flowmeter has been calibrated under controlled pressure and temperature. The read gas flow-rate must be corrected taking into account pressure and temperature variability using the following relations (Perry and Green, 1997):

$$Q_G \left( \text{NL.h}^{-1} \right) = Q_{G,read} \left( \text{NL.h}^{-1} \right) \sqrt{\frac{PT_{calib} \cdot M_{calib}}{P_{calib} \cdot TM}} \text{ and } Q_G \left( \text{L.h}^{-1} \right) = Q_{G,read} \left( \text{L.h}^{-1} \right) \sqrt{\frac{TP_{calib} \cdot M_{calib}}{T_{calib} \cdot PM}} \quad \text{Eq. 13}$$

The subscripts “calib” refers to the conditions used during the calibration. Values of the physico-chemical properties and a list of the suppliers and references of the chemical compounds and equipments used are respectively presented in Tables A.1 and A.2.

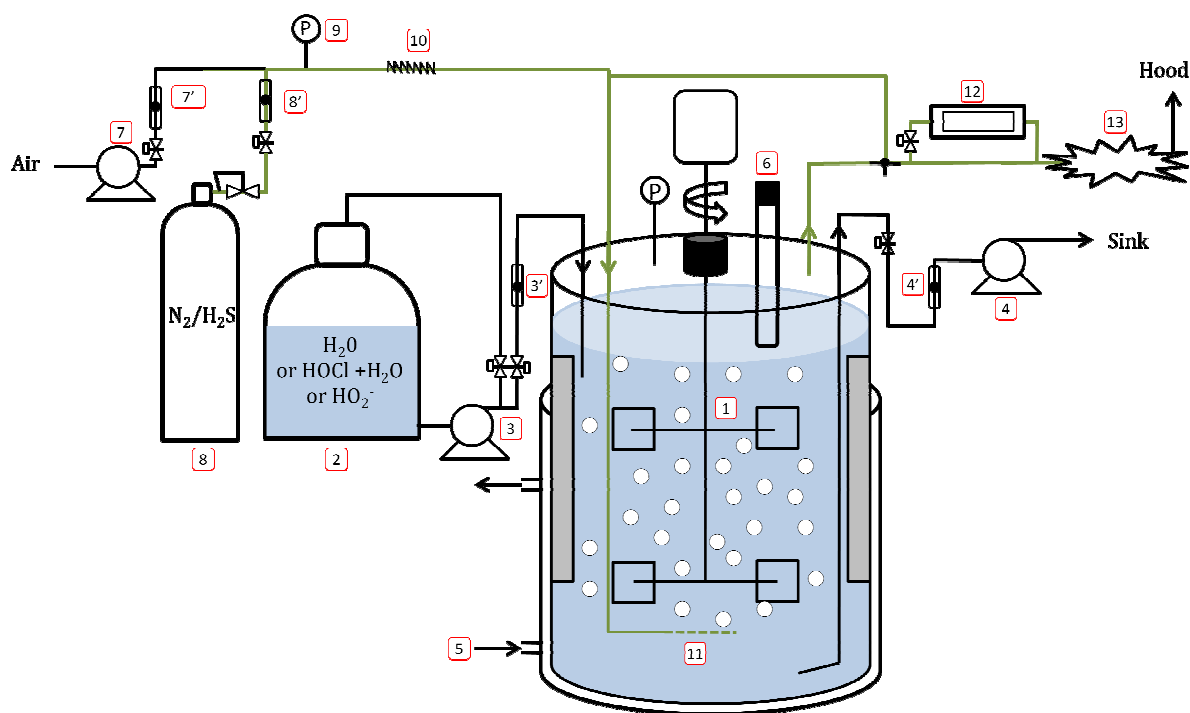


Figure 1: Scheme of the experimental set-up.

## 3.2 Analysis

Chlorine and hydrogen peroxide were analyzed by the iodometric method. An excess of iodide potassium was oxidized in diode at acidic pH (use of HCl for  $\text{H}_2\text{O}_2$  and of  $\text{CH}_3\text{COOH}$  for  $\text{ClOH}$ ) which was titrated by sodium thiosulfate. Ammonium heptamolybdate at  $5 \text{ g L}^{-1}$  was added for  $\text{H}_2\text{O}_2$  analysis to catalyze the  $\text{I}_2$  formation.

$\text{H}_2\text{S}$  in the gas phase was bubbled continuously at a controlled flow rate of  $50 \text{ L h}^{-1}$  (at ambient temperature and pressure) in a  $90 \text{ mL}$  concentrated chlorine solution ( $500 \text{ mg L}^{-1}$ ) at  $\text{pH} = 9$ , and then, oxidized into sulfate ions. Then the sulfates formed were analyzed by ion chromatography with conductivity detection. The  $\text{H}_2\text{S}$  concentration was deduced from the amount of sulfate anion and the volume of gas trapped.

$\text{O}_3$  was analyzed in the gas phase using an UV ozone analyzer. Measurements of dissolved  $\text{O}_3$  and  $\text{H}_2\text{S}$  were not necessary since they were rapidly oxidized in the chemical system implemented and therefore could not be detected. For  $k_G$  determination, a membrane covered galvanic sensor was used to measure dissolved oxygen concentration.

## 4 Results and discussion

### 4.1 Hydrodynamics of the gas-liquid contactor

The assumption of the complete liquid back mixing (perfectly mixed liquid phase) has been checked by Residence Time Distribution (RTD) experiments for various gas (0 to 800 NL h<sup>-1</sup>) and liquid (20 to 80 L h<sup>-1</sup>) flow rates and impeller speed (100 to 800 rpm) using fluorescein as a tracer. It showed that the liquid was perfectly mixed while the impeller speed is larger than 100 rpm whatever the flow rate in the range implemented.

The gas flow pattern cannot be determined by RTD measurement due to a too low residence time (few seconds) which is not compatible with usual sensor time response. However, we can assume that the gas back mixing is almost negligible since the impeller speed is lower than the minimal speed necessary to disperse the gas below the sparger. Indeed, according to the relations cited by Lee and Pang Tsui (1999), a minimal speed of 800-1000 rpm is expected for the gas flow rate range tested. This was confirmed by visual observation. Since the gas loading was rather low, the elevation of the liquid level after starting the gas dispersion was not significant confirming a gas hold-up lower than 1.5%.

The interfacial area  $a^\circ$  can be determined in the pseudo first-order chemical absorption regime (Hoffmann et al., 2007; Rejl et al., 2009). Chemical absorption of ozone in an aqueous solution doped with hydroperoxyde anions HO<sub>2</sub><sup>-</sup> can be satisfactorily used, especially considering that ozone is poorly soluble in water ( $H_A$  is large) which allows to neglect the gas phase resistance ( $R_G \rightarrow 0$  and  $k_L \approx K_L$ ). HO<sub>2</sub><sup>-</sup>, the conjugated base of H<sub>2</sub>O<sub>2</sub>, initiates the O<sub>3</sub> decomposition according to the following bimolecular irreversible reaction (Staehelin and Hoigne, 1982):



If H<sub>2</sub>O<sub>2</sub> is introduced in large amount and at a basic pH, the ozone consumption is fast in the liquid film which means that O<sub>3</sub> does not reach the liquid bulk. Consequently, O<sub>3</sub> is entirely consumed by HO<sub>2</sub><sup>-</sup> and not by any parasite compound or radical formed after its decomposition with the net consumption of one mol of H<sub>2</sub>O<sub>2</sub> for one mol of O<sub>3</sub> transferred (Biard, 2009). Therefore, according to Eq. 11:

$$\ln \frac{C_{\text{O}_3,i}^G}{C_{\text{O}_3,o}^G} = Ek_L a^\circ \frac{VRT}{H_{\text{O}_3} Q_G} \quad \text{Eq. 15}$$

Moreover, since the  $\text{H}_2\text{O}_2$  deprotonation into  $\text{HO}_2^-$  is really faster than ozone consumption by  $\text{HO}_2^-$  and since  $C_{\text{H}_2\text{O}_2} \gg C_{\text{O}_3}^*$ , the  $\text{HO}_2^-$  concentration remains constant in the diffusional film (pseudo first-order absorption regime). In this case (Hikita and Asai, 1964):

$$E = \frac{Ha}{\tanh(Ha)} \quad \text{Eq. 16}$$

Ha (Hatta number) is a dimensionless number:

$$Ha = \sqrt{\frac{k_{\text{O}_3/\text{HO}_2^-} C_{\text{HO}_2^-} D_{\text{O}_3}}{k_L^2}} \quad \text{Eq. 17}$$

$D_i$  is the liquid diffusion coefficient of any species  $i$ . If the reaction kinetics is fast in the liquid film ( $Ha \gg 3$ ),  $\tanh(Ha)$  tends towards 1. Therefore:

$$\ln \frac{C_{A,i}^G}{C_{A,o}^G} = Ha k_L a^\circ \frac{VRT}{H_{\text{O}_3} Q_G} = \sqrt{k_{\text{O}_3/\text{HO}_2^-} [\text{HO}_2^-] D_{\text{O}_3,L}} a^\circ \frac{VRT}{H_{\text{O}_3} Q_G} \quad \text{Eq. 18}$$

Consequently:

$$a^\circ = \frac{-\ln(1 - \text{Eff}_{\text{O}_3})}{\sqrt{k_{\text{O}_3/\text{HO}_2^-} [\text{HO}_2^-] D_{\text{O}_3}}} \frac{Q_G H_{\text{O}_3}}{VRT} \quad \text{Eq. 19}$$

In a given gas-liquid mechanically agitated vessel,  $a^\circ$  depends on the gas flow rate, impeller speed and liquid properties (ionic strength, presence of surfactant). Consequently, these parameters must be controlled. Since  $a^\circ$  does not depend on the absorbed species, extrapolation from  $\text{O}_3$  to  $\text{H}_2\text{S}$  chemical system is not an issue. However, the ionic strength must be kept low to have identical properties between both chemical systems.  $a^\circ$  has been determined for various gas flow rates and  $\text{H}_2\text{O}_2$  concentrations at  $\text{pH} = 10$ . The  $\text{HO}_2^-$  concentration in the contactor was deduced from the pH measured and the  $\text{H}_2\text{O}_2$  concentrations at the inlet, and the mass balance considering that one mol of  $\text{O}_3$  transferred consumed one mol of  $\text{H}_2\text{O}_2$ .

In the thin range of studied superficial velocity,  $a^\circ$  is not statistically dependent on the velocity (Table A.3 in appendix). An average value of  $76.1 \pm 4.9 \text{ m}^2 \text{ m}^{-3}$  is found (Relative Standard Deviation RSD = 6%). The average value of  $a^\circ$  is in agreement with the order of magnitude expected. The standard deviation stays within the calculated 10% experimental uncertainty. The parity plot (Fig. 2) confirms a good agreement between the experimental and theoretical (using Eq. 19 and  $a^\circ = 76.1 \text{ m}^2 \text{ m}^{-3}$ )  $\text{Eff}_{\text{O}_3}$  values. The values of the Hatta number, using the  $k_L$  value measured later (§ 4.2), are larger than 3, confirming the fast reaction assumption (Table A.3 in appendix).

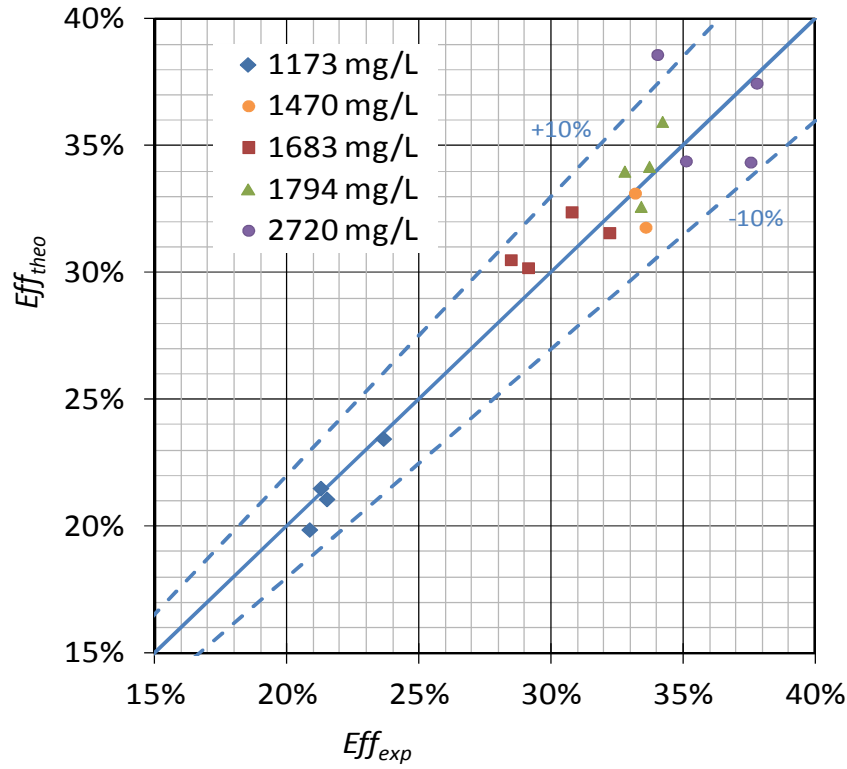


Figure 2: Parity diagram comparing the experimental values of the ozone removal efficiency with the theoretical values obtained with  $\alpha^\circ = 76.1 \text{ m}^2 \text{ m}^{-3}$  for various  $\text{H}_2\text{O}_2$  concentrations.

## 4.2 Liquid-side mass transfer coefficient determination

The liquid side mass transfer coefficient  $k_L$  depends on the absorbed species diffusion coefficient, the liquid properties (viscosity, density) and the liquid hydrodynamics.  $k_L$  can be determined by chemical or physical methods (Hoffmann et al., 2007; Rejl et al., 2009). Chemical methods results can be biased by the reactant added which can affect the liquid properties. The only restriction linked to the physical absorption method is the requirement of a poorly soluble compound to avoid reaching the gas-liquid equilibrium and limit the gas-phase resistance ( $R_G \rightarrow 0$ ) (Lara Marquez et al., 1994). Consequently, the physical absorption of pure oxygen at steady-state has been selected. In this case:

$$C_{O_2,i}^{Eq} = C_{O_2,o}^{Eq} = \frac{p_{O_2}}{H_{O_2}} \quad \text{Eq. 20}$$

Therefore, since the liquid phase is perfectly mixed, the driving force is constant in the whole volume of the gas-liquid contactor:

$$\overline{(C_{O_2}^{Eq} - C_{O_2})} = \frac{p_{O_2}}{H_{O_2}} - C_{O_2,o} \quad \text{Eq. 21}$$

The mass transfer equation (Eq. 8) coupled with the mass balance equation leads to Eq. 22:

$$N = k_L a^\circ V \left( \frac{p_{O_2}}{H_{O_2}} - C_{O_2,o} \right) = Q_L (C_{O_2,o} - C_{O_2,i}) \quad \text{Eq. 22}$$

$$\Rightarrow k_L = \frac{Q_L (C_{O_2,o} - C_{O_2,i})}{a^\circ V \left( \frac{p_{O_2}}{H_{O_2}} - C_{O_2,o} \right)} \quad \text{Eq. 23}$$

$Q_L$  is the liquid volume flow rate ( $\text{m}^3 \text{s}^{-1}$ ).  $\frac{p_A}{H_{O_2}}$  corresponds to the  $O_2$  concentration at saturation in

the liquid which can be measured in the semi-continuous mode waiting for the saturation. No significant effect of the gas and liquid flow rates on  $k_L$  has been emphasized (Table 2). An average value of  $k_L^{O_2} = 2.7 \times 10^{-4} \pm 0.25 \times 10^{-4} \text{ m s}^{-1}$  (RSD = 9%) was found which is totally in agreement with the expected value. The  $H_2S$  liquid side mass transfer coefficient must be extrapolated from the oxygen one by the following relation (Roustan, 2003):

$$\frac{k_L^{H_2S}}{k_L^{O_2}} = \sqrt{\frac{D_{H_2S}}{D_{O_2}}} \Rightarrow k_L^{H_2S} = 2.5 \times 10^{-4} \pm 0.2 \times 10^{-4} \text{ m s}^{-1} \quad \text{Eq. 24}$$

Table 2: Results of the oxygen absorption experiments.

$Q_G$ (NL h <sup>-1</sup> )	426	426	469	469	469	509	509	509
$U_{SG}$ (cm s <sup>-1</sup> )	1.24	1.24	1.37	1.37	1.37	1.49	1.49	1.49
$Q_L$ (L h <sup>-1</sup> )	21.2	28.6	13.9	21.2	28.6	13.9	21.2	28.6
$10^4 \times k_L$ (m s <sup>-1</sup> )	2.29	2.55	2.43	2.89	2.80	2.89	2.79	2.98

### 4.3 Gas-side mass transfer coefficient determination

To measure the gas side coefficient, the liquid resistance must be negligible ( $R_L \rightarrow 0$ ) which is the case when  $E$  is very large due to a very fast chemical reaction with a large excess of the reagents. Moreover, the solute is instantaneously consumed at the gas-liquid interface ( $C_A = 0$ ). According to Eq. 11 :

$$\ln \frac{C_{A,i}^G}{C_{A,o}^G} = \frac{k_G a^\circ V}{Q_G} \Rightarrow k_G = -\frac{Q_G}{a^\circ V} \ln(1 - Eff) \quad \text{Eq. 25}$$

$k_G$  has been measured by  $H_2S$  absorption in an alkaline chlorine solution ( $10.5 < \text{pH} < 11$  and  $C_{ClOH} = 1 \text{ g L}^{-1}$ ) for various gas and liquid flow rates ( $500 < Q_G < 550 \text{ NL h}^{-1}$ ). No significant effect of the flow rates on  $k_G$  has been emphasized. An average value of  $k_G = 4.2 \times 10^{-3} \pm 0.33 \times 10^{-3} \text{ m s}^{-1}$  (RSD = 8%) was found.

The  $k_G$  value is a rather low and comparable to the values found in packed or spraying columns. Since it has never been measured for a mechanically agitated vessel, there is no possibility to discuss the validity of this result. In the case of  $H_2S$ , which is rather poorly soluble in water, the mass transfer resistance in the gas side ( $R_G$ ) must not be neglected, especially with increasing  $E$  values in the liquid phase (Fig. 3). This result is very important for the following step. Indeed, the enhancement factor obtained during the  $H_2S$  absorption in chlorine solution should not be too large to limit as much as possible the gas-side resistance and improve the sensitivity of the calculations.

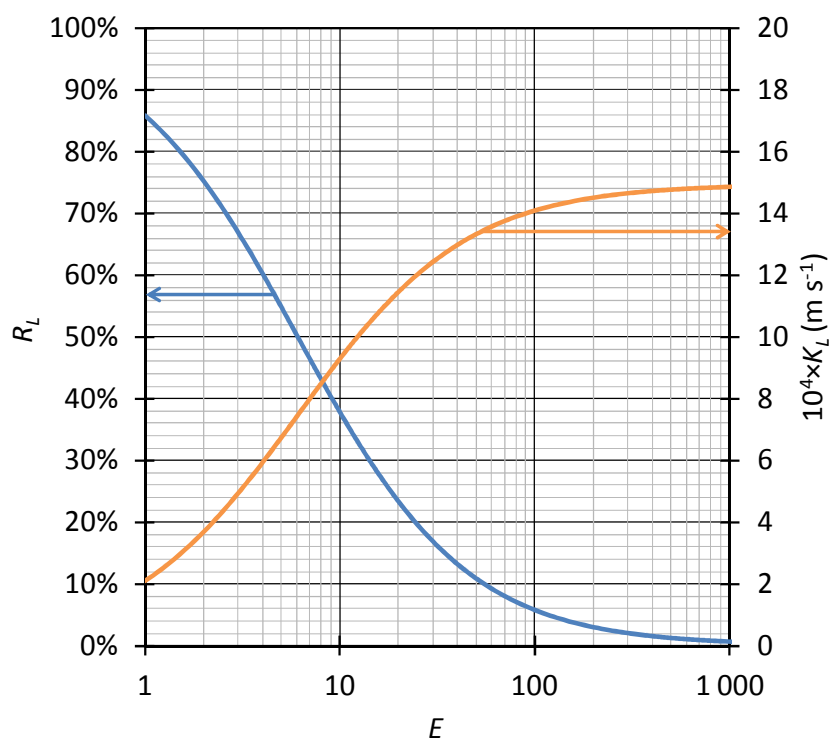


Figure 3: Liquid-phase relative mass transfer resistance  $R_L$  and overall liquid-phase mass transfer coefficient  $K_L$  vs. the enhancement factor  $E$ .

## 4.4 Validation of the mass transfer and hydrodynamic parameters

### 4.4.1 $H_2S$ absorption in slightly alkaline water

The accuracy of  $\alpha^\circ$ ,  $k_L$  and  $k_G$  values has been evaluated for  $H_2S$  absorption in water at alkaline pH (NaOH was added) using the operating conditions synthesized in Table 1. The pH was slightly alkaline to improve the  $H_2S$  removal efficiency (>20%) at a level sufficient to limit the experimental uncertainty.

Without  $H_2S$  oxidation and assuming that  $S^{2-}$  is negligible at the working pH,  $C_A$  can be deduced from the mass balance equation:



$$N = Q_G (C_{H_2S,i}^G - C_{H_2S,o}^G) = Q_L C_{H_2S} (1 + 10^{pH - pK_{A,2}}) \quad \text{Eq. 26}$$

According to Eqs 11 and 26:

$$\ln \left( \frac{A(1 + 10^{pH - pK_{A,2}}) - Eff_{H_2S}}{A(1 + 10^{pH - pK_{A,2}})(1 - Eff_{H_2S}) - Eff_{H_2S}} \right) = K_L a^\circ \frac{AV}{Q_L} \quad \text{Eq. 27}$$

A is the absorption rate (no unit) defined by Eq 28:

$$A = \frac{Q_L RT}{Q_G H_{H_2S}} \quad \text{Eq. 28}$$

This equation provides a limit value of  $Eff_{H_2S}$  since the term in the logarithm must be positive:

$$Eff_{\max} = \frac{A(1 + 10^{pH - pK_{A,2}})}{1 + A(1 + 10^{pH - pK_{A,2}})} \quad \text{Eq. 29}$$

$Eff_{\max}$  is obtained when the chemical equilibrium is reached between the gas at the outlet and the liquid. It is the maximal removal efficiency for given pH, temperature and gas and liquid flow rates.

Finally, from Eq. 29:

$$Eff_{H_2S} = \frac{A(1 + 10^{pH - pK_{A,2}}) \left( 1 - \exp \left( K_L a^\circ \frac{AV}{Q_L} \right) \right)}{1 - \left( A(1 + 10^{pH - pK_{A,2}}) + 1 \right) \exp \left( K_L a^\circ \frac{AV}{Q_L} \right)} \quad \text{Eq. 30}$$

H<sub>2</sub>S mass transfer in water can be enhanced thanks to the H<sub>2</sub>S dissociation ( $E_{\text{diss}}$ ) and/or recombination with HO<sup>-</sup> ( $E_{\text{HO}^-}$ ) which form HS<sup>-</sup> in the liquid film (Biard and Couvert, 2013). This phenomenon is highly influenced by the pH. Assuming that these reactions are instantaneous comparing to mass transfer, the enhancement factors for each reaction can be calculated for each experimental point (Biard and Couvert, 2013). The global enhancement factor can be calculated for 2 instantaneous reactions by the sum of the individual enhancement factor minus 1 (Chang and Rochelle, 1982; van Swaaij and Versteeg, 1992). Then, it leads to:

$$\begin{aligned} E_\infty &= E_{\text{HO}^-} + E_{\text{diss}} - 1 \\ E_{\text{HO}^-} &= 1 + \frac{D_{\text{HO}^-} 10^{pH - pK_w}}{\frac{D_{H_2S} D_{\text{HO}^-}}{D_{\text{HS}^-} \times 10^{pK_w - pK_{A,2}}} + D_{H_2S} C_{H_2S}^*} \\ E_{\text{diss}} &= 1 + \frac{\sqrt{(D_{H^+} 10^{-pH} + D_{\text{HS}^-} C_{\text{HS}^-})^2 - 4(1 - C_{H_2S}^*/C_{H_2S})(D_{H^+} 10^{-pH} D_{\text{HS}^-} C_{\text{HS}^-}) - (D_{H^+} 10^{-pH} + D_{\text{HS}^-} C_{\text{HS}^-})}}{2D_{H_2S}(C_{H_2S}^* - C_{H_2S})} \end{aligned} \quad \text{Eq. 31}$$

$\text{pk}_w$  is the negative log of the water ion product. The dissociation enhancement factor is low and included in the range 1.01-1.05 while the recombination with  $\text{HO}^-$  enhancement factor is in the range 1.18-1.29.

Comparison between the experimental removal efficiency and the theoretical values deduced from Eqs 30 and 31 is really good (Fig. 4). For low values of A, the equilibrium is almost reached since the removal efficiency is rather close of the maximal removal efficiency obtained from Eq. 29.

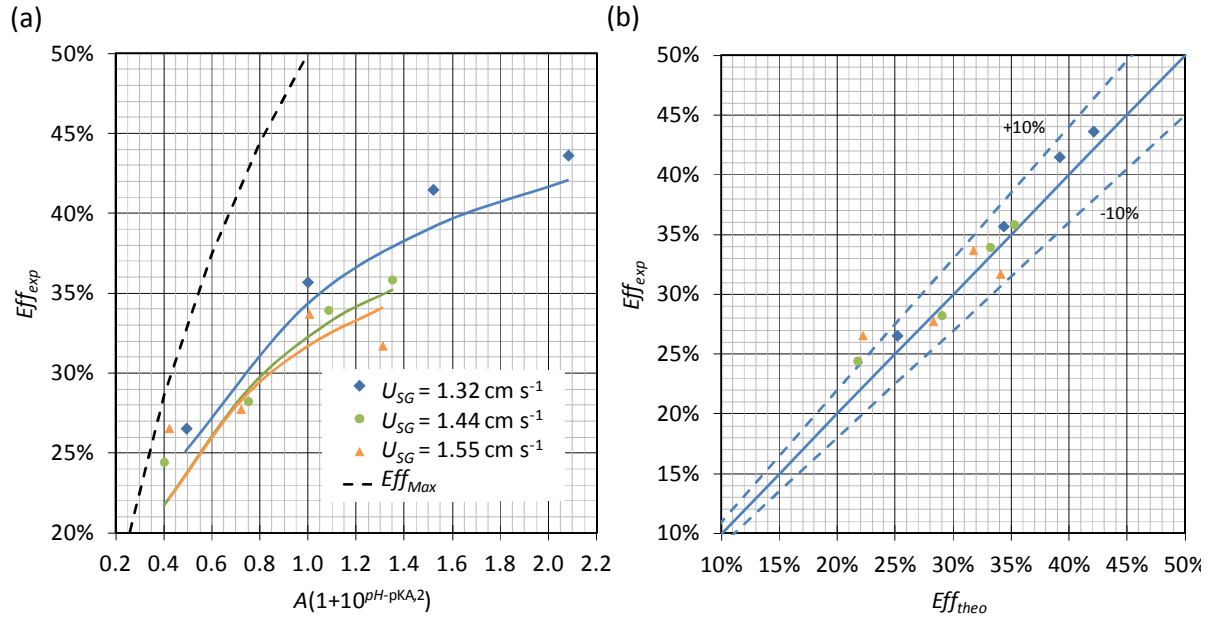


Figure 4: (a).  $\text{H}_2\text{S}$  removal efficiency vs.  $A(1+10^{\text{pH}-\text{pK}_{A,2}})$  for various gas flow rates without chlorine. The colored lines represent the prediction of the model (Eq. 30) and the black line represents the prediction of the maximal removal efficiency (Eq. 29). (b). Parity plot between the experimental and predicted removal efficiencies.

#### 4.4.2 Sensitivity analysis

The good agreement between the experimental and the theoretical values is not a sufficient condition to confirm the accuracy of the mass transfer coefficients and interfacial area determined previously and the robustness of the model. Indeed, each parameter has a variable influence on the removal efficiency. This influence can be assessed through a sensitivity analysis based on the elasticity index determination. The sensitivity analysis quantifies the effect of possible change in inputs on the model output which is here the removal efficiency (Asadi Kalameh et al., 2012; Yin et al., 2005). Consequently, it addresses the relative significance of potential errors in various input parameters. The elasticity index  $\text{EI}_{\text{P}/\text{Eff}}$  measures the relative change of the removal efficiency for a relative change in an input parameter P. For example, for the input  $k_L$  :

$$\text{EI}_{k_L/\text{Eff}} = \frac{k_L}{\text{Eff}_{\text{for } k_L}} \times \frac{1}{2} \left[ \frac{\text{Eff}_{\text{for } k_L + \Delta k_L} - \text{Eff}_{\text{for } k_L}}{\Delta k_L} + \frac{\text{Eff}_{\text{for } k_L - \Delta k_L} - \text{Eff}_{\text{for } k_L}}{-\Delta k_L} \right] \quad \text{Eq. 32}$$

$Eff_{H_2S}$  must be a monotonic function of the input parameter  $P$ . The average elasticity indexes, taking into account all the experimental points, have been estimated for all the input of Eq. 30 for a relative change of 10% (Table 3). The indexes for the input  $Q_G$  and  $H_{H_2S}$  are negative since  $Eff$  is a decreasing function of *them*. Except for the  $pH$ , the standard deviation is low, demonstrating that EI is almost constant. Results of Table 3 emphasize that  $Eff$  is mainly sensitive to two measured variables,  $pH$  and  $Q_G$ , and two physico-chemical constants,  $pK_{A,2}$  and  $H_{H_2S}$ , whose the values taken from the literature are consistent between many authors and should be precise. Consequently, the difference between the experimental and the theoretical values of  $Eff_{H_2S}$  (Fig. 4) might be mainly due to the experimental errors of the  $pH$ , and in a lower extent of  $Q_G$ , more than uncertainties of  $k_L$ ,  $k_G$  and  $\alpha^\circ$  determined previously. On the one hand,  $pH$  was rather unsteady and affected by the gas bubbles with a low precision of  $\pm 0.1$  unit. On the other hand,  $Q_G$  was measured with a limited combined uncertainty of 3.1% taking into account the uncertainties of the variable area flowmeter, the pressure and the temperature measurements used for the flow rate correction. The strong sensitivity of  $Eff$  to the  $pH$  and  $pK_{A,2}$  can be explained by the fact that these inputs affect significantly the difference of  $H_2S$  concentrations between the interface and the bulk (mass transfer driving force).

**Table 3: Elasticity index determination for  $Eff_{H_2S}$  and  $K_L\alpha^\circ$ .**

Removal efficiency ( $Eff_{H_2S}$ )								
Input parameter	$pH$	$pK_{A,2}$	$Q_G$	$H_{H_2S}$	$\alpha^\circ$ and $V$	$E$ and $k_L$	$Q_L$	$k_G$
Average EI	4.83	2.30	-0.81	-0.73	0.45	0.37	0.36	0.079
Standard deviation	1.42	0.93	0.04	0.05	0.07	0.06	0.11	0.013
Overall liquid mass transfer coefficient ( $K_L\alpha^\circ$ )								
Input parameter	$E$ and $k_L$					$k_G$		
Average EI	0.83					0.17		
Standard deviation	0.004					0.004		

The removal efficiency ( $Eff_{H_2S}$ ) is also significantly influenced by  $\alpha^\circ$  and  $V$  (which possesses a low experimental uncertainty of 3.0%), proving the  $\alpha^\circ$  value determined previously is coherent and confirming the order of magnitude. The EI determination for  $E$  and  $k_L$  shows that  $Eff_{H_2S}$  is moderately sensitive to these parameters. Consequently, the order of magnitude of  $E$  and  $k_L$  should be coherent. On the contrary,  $Eff_{H_2S}$  is almost independent of  $k_G$  since the gas phase resistance is low (15% for  $E$  close to 1 according to Fig. 3). This is confirmed by the sensitivity index calculation of  $K_L\alpha^\circ$  for the input  $k_G$  ( $EI_{k_L\alpha/k_G}$ ) which is 5 times lower than  $EI_{k_L\alpha/k_L}$  and  $EI_{k_L\alpha/E}$  (Table 3). By the way, the  $k_G$  value found previously cannot be validated. To limit the influence of this uncertainty on the  $E$  determination using chlorine, the gas-phase resistance should be kept low as demonstrated by Fig. 3.

Moreover, Fig. 3 highlights an asymptotic behavior which emphasizes that  $K_L a^\circ$  becomes less sensitive to  $E$  when  $E$  increases which could affect the uncertainty of the kinetic study.

## 4.5 Oxidation kinetics investigation

### 4.5.1 Enhancement factor determination

Table 4: Results of the H<sub>2</sub>S reactive absorption in chlorine solutions.

pH	C <sub>NaOCl</sub> (ppm)	C <sub>H<sub>2</sub>S</sub> <sup>G</sup> (10 <sup>3</sup> mol m <sup>-3</sup> )	y <sup>†</sup> (%)	E <sub>exp</sub>	E <sub>theo</sub>	E <sub>39</sub> /E <sub>39+40</sub> <sup>‡</sup> (%)	Eff <sub>exp</sub> (%)	Eff <sub>theo</sub> (%)	Error (%)
4.90	293	1.50	84.3	7.0	5.41	38.5	89.0	85.6	4.0
4.92	301	1.65	83.2	6.4	5.49	38.8	88.0	86.1	2.3
4.93	305	1.43	85.3	7.5	5.55	39.5	89.7	86.0	4.3
4.94	222	2.50	73.9	3.6	4.69	38.6	79.3	84.3	5.9
4.95	229	2.38	75.2	3.8	4.78	39.1	80.4	84.4	4.8
4.95	233	2.01	78.5	4.8	4.83	39.7	83.6	83.8	0.2
5.59	278	1.19	88.6	4.2	6.64	67.4	79.4	86.8	8.5
5.59	282	1.25	88.1	3.9	6.66	67.0	78.1	86.8	10.0
5.58	284	1.28	87.9	3.8	6.66	66.7	77.8	86.9	10.5
5.80	45	2.17	70.0	2.3	2.86	74.8	68.7	74.4	7.8
5.88	170	2.05	80.6	5.2	6.01	76.9	85.1	87.2	2.4
5.88	178	2.12	80.4	5.0	6.15	76.8	84.3	87.5	3.5
5.88	182	2.07	80.9	5.2	6.23	76.9	85.2	87.8	3.0
5.99	351	1.78	87.8	9.6	9.64	82.1	90.0	90.1	0.0
5.99	365	1.72	88.3	10.0	9.85	82.2	90.3	90.2	0.1
6.04	202	1.21	90.1	9.6	7.76	84.5	92.0	90.1	2.1
6.50	187	1.47	91.2	6.9	11.25	93.8	88.7	93.1	4.7
6.51	191	1.45	91.5	7.0	11.48	94.0	88.9	93.2	4.6
6.94	269	0.39	98.6	27.8	21.13	97.9	96.6	95.9	0.7
7.53	257	0.46	98.9	23.6	32.10	99.4	96.2	96.8	0.7
7.53	265	0.25	99.4	44.1	32.67	99.4	97.3	96.8	0.4

Chemical absorption of H<sub>2</sub>S was realized at various chlorine concentration and  $pH$  (Table 4). Since the H<sub>2</sub>S oxidation rate is higher than the H<sub>2</sub>S mass transfer rate and the Damköhler number is large (10 to 30),  $C_A$  can be neglected comparing to  $C_A^{Eq}$  (Roustan). In this case, according to Eq. 11,  $K_L a^\circ$  and  $E_{exp}$  can be deduced for each experiment by respectively Eqs 33 and 7:

$$\ln \frac{C_{H_2S,i}^G}{C_{H_2S,o}^G} = K_L a^\circ \frac{VRT}{H_{H_2S} Q_G} \Rightarrow K_L a^\circ = - \frac{H_{H_2S} Q_G}{VRT} \ln(1 - Eff_{H_2S}) \quad \text{Eq. 33}$$

<sup>†</sup> x was comprised between 0.98 and 1.00 demonstrating that the reaction with ClOH is pseudo-first order.

<sup>‡</sup> Represents the ratio of E obtained considering only the reaction 39 on E considering both reactions 39 and 40.

The results show that  $E_{exp}$  (i.e. the oxidation kinetic rate) increases obviously with the chlorine concentration but also surprisingly with the pH. Indeed, ClOH is considered as more reactive than  $ClO^-$  which lets expect a larger kinetic rate for lower pH. It might emphasize that  $HS^-$  plays a role in the oxidation mechanism, even if at the implemented pH, the  $HS^-$  concentration is significantly lower than the  $H_2S$  concentration. We note that  $E_{exp}$  values were included in the range 2.3-44, confirming that  $H_2S$  is entirely consumed in the liquid film for most experiments.

#### 4.5.2 Kinetic constants determination

According to the experimental results, the oxidation mechanism might involve both acid-base and oxidation reactions. Indeed,  $H_2S$  and  $HS^-$  can be both oxidized by  $ClO^-$  or ClOH. A list of the potential reactions is presented in Table 5.

According to Eigen (1964),  $k_1$  and  $k_3$  values should be close to  $3 \times 10^{10}$  and  $10^9$  L mol<sup>-1</sup> s<sup>-1</sup>. The increasing of the kinetic rate with the pH can be due to the fact that a part of  $H_2S$  reacts with  $ClO^-$  in the liquid film to form  $HS^-$  (reaction 36) which can be further oxidized by ClOH (oxidation with  $ClO^-$  is unexpected according to the order of magnitude of  $k_4$  and  $k_5$ ). Moreover, ClOH can oxidize directly  $H_2S$ . If we assume that reverse reaction 36 is negligible, then the whole mechanism can be reduced to the two irreversible reactions 39 (equivalent to reaction 36 followed by reaction 37) and 40; and the two kinetic constants  $k_6$  and  $k_7$  must be determined.

**Table 5 :  $H_2S$  oxidation mechanism.  $k_2$  value and  $k_1$  and  $k_3$  orders of magnitude were obtained from (Eigen, 1964).  $k_4$  and  $k_5$  orders of magnitude were obtained from (Deborde and von Gunten, 2008).**

Reaction	Type	Equilibrium constant
$H_2S + HO^- \xrightleftharpoons[k_{-1} \approx 2.4 \cdot 10^3 \text{ s}^{-1}]{k_1 \approx 3 \cdot 10^{10} \text{ L mol}^{-1} \text{ s}^{-1}} HS^- + H_2O$	Eq. 34    Acid-base	$K = \frac{k_1}{k_{-1}} = 10^{-pK_{A,2} + pK_w}$
$H_2S + H_2O \xrightleftharpoons[k_{-2} = 7.5 \cdot 10^{10} \text{ L mol}^{-1} \text{ s}^{-1}]{k_2 = 6.24 \cdot 10^3 \text{ s}^{-1}} HS^- + H^+ + H_2O$	Eq. 35    Acid-base	$K = \frac{k_2}{k_{-2}} = 10^{-pK_{A,2}}$
$H_2S + ClO^- \xrightleftharpoons[k_{-3} \approx 3 \cdot 10^8 \text{ L mol}^{-1} \text{ s}^{-1}]{k_3 \approx 10^9 \text{ L mol}^{-1} \text{ s}^{-1}} HS^- + ClOH$	Eq. 36    Acid-base	$K = \frac{k_3}{k_{-3}} = 10^{pK_{A,1} - pK_{A,2}}$
$HS^- + ClOH \xrightarrow{k_4 \approx 5 \cdot 10^8 \text{ L mol}^{-1} \text{ s}^{-1}} S + Cl^- + H_2O$	Eq. 37 $HS^-$ oxidation	
$HS^- + ClO^- \xrightarrow{k_5 \approx 10^4 \text{ L mol}^{-1} \text{ s}^{-1}} S + Cl^- + HO^-$	Eq. 38 $HS^-$ oxidation	
$H_2S + ClO^- \xrightarrow{k_6} S + Cl^- + H_2O$	Eq. 39 $H_2S$ oxidation	
$H_2S + ClOH \xrightarrow{k_7} S + HCl + H_2O$	Eq. 40 $H_2S$ oxidation	

The enhancement factor for two irreversible parallel reactions in the liquid film can be determined using the Onda and coworkers approximated solution for the two-film theory (Biard et al., 2010; Onda et al., 1970). From the material balances and the boundary conditions:

$$E = \frac{1 - \frac{C_{H_2S}}{C_{H_2S}^*} + \frac{C_{ClOH}}{C_{H_2S}^*} \left[ \frac{D_{ClOH}}{D_{H_2S}} \left( 1 - \frac{C_{ClOH}^*}{C_{ClOH}} \right) + \frac{D_{ClO^-}}{D_{H_2S}} \left( \frac{C_{ClO^-}}{C_{ClOH}} - \frac{C_{ClO^-}^*}{C_{ClOH}} \right) \right]}{1 - C_{H_2S}/C_{H_2S}^*} \quad \text{Eq. 41}$$

Due to the fast oxidation of  $H_2S$  in solution, the bulk concentration is negligible compared to the interface concentration:

$$E = 1 + \frac{C_{ClOH}}{C_{H_2S}^*} \left[ \frac{D_{ClOH}}{D_{H_2S}} \left( 1 - \frac{C_{ClOH}^*}{C_{ClOH}} \right) + \frac{D_{ClO^-}}{D_{H_2S}} \left( \frac{C_{ClO^-}}{C_{ClOH}} - \frac{C_{ClO^-}^*}{C_{ClOH}} \right) \right]$$

$$\Rightarrow E = 1 + \frac{D_{ClOH}}{D_{H_2S}} \frac{C_{ClOH}}{C_{H_2S}^*} (1-x) + \frac{D_{ClO^-}}{D_{H_2S}} \frac{C_{ClO^-}}{C_{H_2S}^*} (1-y) \quad \text{with } x = \frac{C_{ClOH}^*}{C_{ClOH}} \text{ and } y = \frac{C_{ClO^-}^*}{C_{ClO^-}}$$
Eq. 42

Onda et al. (1970) proposed an approximate solution of the differential equations system obtained by linearization. For two second-order reactions:

$$E = \frac{\sqrt{M_2} \left( 1 - \frac{C_{H_2S}}{C_{H_2S}^*} \frac{1}{\cosh(\sqrt{M_2})} \right)}{(1 - C_{H_2S}/C_{H_2S}^*) \tanh(\sqrt{M_2})} \approx \frac{\sqrt{M_2}}{\tanh(\sqrt{M_2})} \quad \text{Eq. 43}$$

With:

$$M_2 = \frac{k_7 D_{H_2S} C_{ClOH}}{k_L^2} \left( x + \frac{k_6}{k_7} \frac{C_{ClO^-}}{C_{ClOH}} y \right) \quad \text{Eq. 44}$$

Eqs. 42 and 43 are two independent equations with 3 variables ( $x$ ,  $y$  and  $E$ ). Therefore, an additional equation is required. Onda et al. (1970) assumed that the reagent concentrations are quadratic functions of the film thickness and obtained the following equation:

$$y = \frac{1 - \frac{1}{6} \frac{D_{ClOH}}{D_{ClO^-}} \frac{k_6}{k_7} (1-x)}{1 + \frac{5}{6} \frac{D_{ClOH}}{D_{ClO^-}} \frac{k_6}{k_7} \frac{1-x}{x}} \quad \text{Eq. 45}$$

Following the numerical procedure developed in the supplementary material,  $k_6$  ( $6.75 \cdot 10^6 \text{ L mol}^{-1} \text{ s}^{-1}$ ) and  $k_7$  ( $1.62 \cdot 10^5 \text{ L mol}^{-1} \text{ s}^{-1}$ ) were determined by the least square method trying to minimize the error between the experimental and theoretical values of  $E$  (procedure presented in the supplementary material). These values confirm the order of magnitude expected by Biard et al. (Biard et al., 2010). The determined apparent kinetic constant of  $H_2S$  with  $ClO^-$  is larger than the one with  $ClOH$  which

corroborates the assumption that  $\text{H}_2\text{S}$  can react with  $\text{ClO}^-$  through an acid base reaction before oxidation. To assess the importance of both reactions with  $\text{ClO}^-$  and  $\text{ClOH}$ , the ratio ( $E_{39}/E_{39+40}$ ) of the enhancement factor calculated assuming just the reaction with  $\text{ClO}^-$  on the overall enhancement factor has been calculated (Table 4). It confirms that, except for circumneutral and basic pH, both reactions contribute to the overall mass transfer enhancement.

The relative errors between the experimental and theoretical values of  $Eff_{\text{H}_2\text{S}}$  are summarized in Table 4 and confirm a rather good agreement of the model. In the one hand, the discrepancy between the experimental and theoretical values of  $E$  is rather large (average error of 24%) since the determination of  $E$  is very sensitive to the experimental uncertainties (on  $Eff$ ,  $Q_G$  and the  $pH$  especially). In other words, even low experimental uncertainties induce a rather large uncertainty on  $E$ . However, the points are distributed on both sides of the parity plot excluding systematic errors (Fig. 5). On the other hand, calculations of theoretical values of  $Eff_{\text{H}_2\text{S}}$  are poorly sensitive to  $E$ . By the way, the difference between the experimental and theoretical values of  $Eff_{\text{H}_2\text{S}}$  is really low (3.8% in average). These observations are emphasized by the sensitivity analysis (§ 4.5.3).

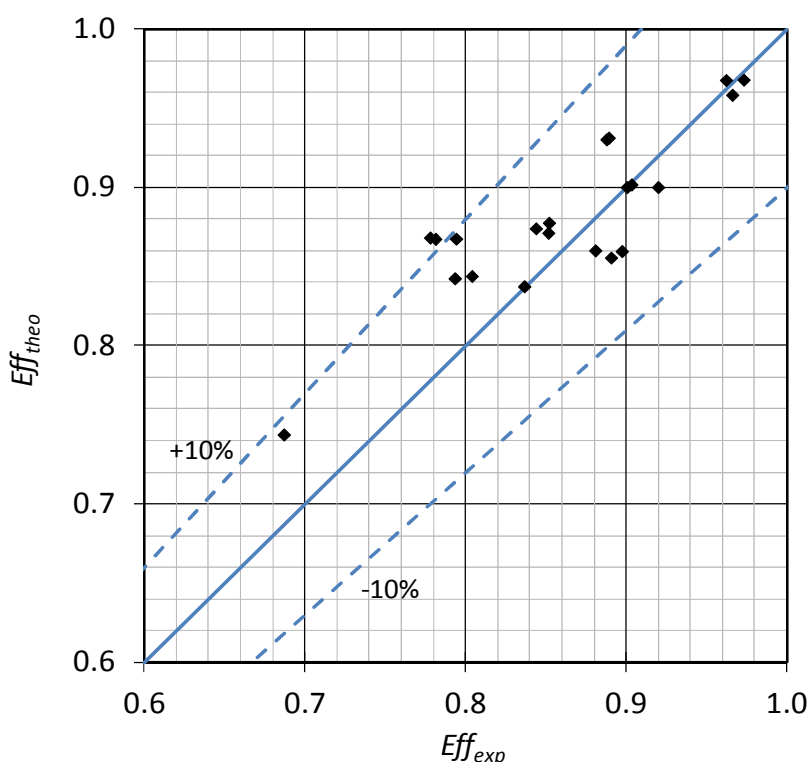


Figure 5: Parity plot between the experimental and predicted removal efficiencies during  $\text{H}_2\text{S}$  absorption in chlorine solutions.

At basic pH, reaction 34 should not be neglected anymore. A competition between Eq. 34 and 36 is expected depending on the pH and the total chlorine concentration. In the next step of this project,  $k_6$  and  $k_7$  will be confronted to the kinetic constants that we measured for  $\text{HS}^-$  oxidation by chlorine

(result not published yet) to build a kinetic model at basic pH. More complex numerical resolution tools will be required to solve the high numbers of differential equations and finally build a model which can provide an efficient tool for scrubbers design.

#### 4.5.3 Sensitivity analysis

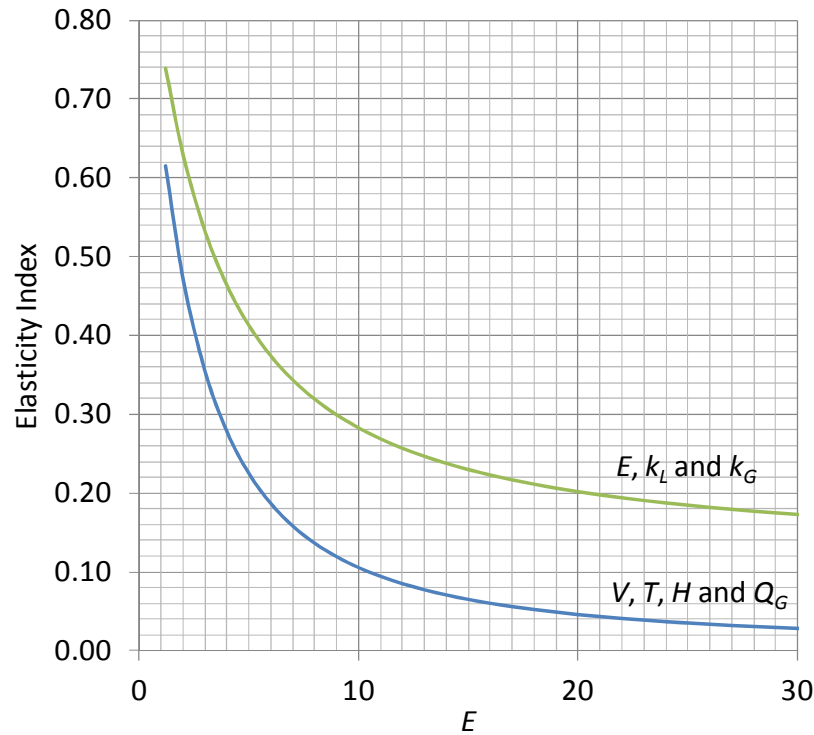


Figure 6: The  $Eff_{H_2S}$  Elasticity Index vs. the enhancement factor for several inputs.

The sensitivity analysis quantifies the influence of the input  $E$ ,  $k_L$ ,  $k_G$ ,  $V$  and  $T$  on the output  $Eff_{H_2S}$  (Fig. 6) for increasing values of  $E$ . The three most significant inputs are  $E$ ,  $k_L$  and  $k_G$  which directly influence the mass transfer rate. Errors on the enhancement factor determination (due to uncertainties on  $k_6$  and  $k_7$ ) are more significant for low values of  $E$  with more liquid phase resistance. With significant chlorine concentrations up to 500 ppm at alkaline pH, the kinetics of oxidation is so large that the resistance in the liquid phase is almost negligible and the mass transfer rate is controlled by the gas phase. This conclusion obtained with a well agitated reactor can be extrapolated to packed column widely used in gas treatment. Therefore, designers must adjust their concentration to insure an excess of chlorine in order to maintain a low liquid phase resistance in the whole gas-liquid contactor, especially at the bottom where chlorine has been partly consumed.



## 5 Conclusions

Kinetics of H<sub>2</sub>S reaction with hypochlorite anion and hypochlorous acid was investigated by reactive absorption in a well agitated gas-liquid contactor. The liquid and gas sides mass transfer coefficients as well as the interfacial area has been determined using appropriated experimental conditions. These values were confirmed with the modeling of reactive absorption of H<sub>2</sub>S in water without oxidant. Absorption of H<sub>2</sub>S in chlorine solutions demonstrated that the oxidation kinetic rate increases surprisingly with the pH which highlights that HS<sup>-</sup> may play a role in the oxidation mechanism. We assumed that H<sub>2</sub>S reacts with ClO<sup>-</sup> to form HS<sup>-</sup> which is further oxidized by ClOH to build a global mechanism based on the H<sub>2</sub>S irreversible reactions with ClO<sup>-</sup> ( $k_6 = 6.75 \cdot 10^6 \text{ L mol}^{-1} \text{ s}^{-1}$ ) and ClOH ( $k_7 = 1.62 \cdot 10^5 \text{ L mol}^{-1} \text{ s}^{-1}$ ). A good agreement between the experimental and the theoretical values of the removal efficiencies confirmed the order of magnitude of the kinetic constants found and the validity of the model at the pH range tested. The next step of this study will require to improve the model for the description of the mechanism at basic pH.

## 6 Acknowledgements

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# Appendix A: Additional tables

Table A. 1 : Compilation of the physico-chemical properties used.

Parameter	Values at 293 K	References
<b>Water</b>		
$\rho_L$ (kg m <sup>-3</sup> )	1000	
$M_L$ (kg mol <sup>-1</sup> )	0.018	
$pK_w$	14.15	
<b>H<sub>2</sub>S</b>		
$H_{H_2S}$ (Pa m <sup>3</sup> mol <sup>-1</sup> )	864	(Fernández-Prini et al., 2003)
$D_{H_2S}$ (m <sup>2</sup> s <sup>-1</sup> )	$1.75 \times 10^{-9}$	(Tamimi et al., 1994)
$pK_{A,2}$ (H <sub>2</sub> S/HS <sup>-</sup> )	$-\log\left(0.00361 \exp\left(-\frac{3131}{T}\right)\right) \Rightarrow 7.07$ at 293 K	(Roustan, 2003)
$pK_{A,3}$ (HS <sup>-</sup> /S <sup>2-</sup> )	$-\log\left(\exp\left(-7.489 - \frac{7211.2}{T}\right)\right) \Rightarrow 13.94$ at 293 K	(Brettschneider et al., 2004)
<b>O<sub>3</sub></b>		
$H_{O_3}$ (Pa m <sup>3</sup> mol <sup>-1</sup> )	$\exp\left(22.3 - \frac{4030}{T}\right) \times 1.013 \times 10^5 \times \frac{M_L}{\rho_L} = 9400$ Pa.m <sup>3</sup> .mol <sup>-1</sup>	(Langlais et al., 1991)
$D_{O_3}$ (m <sup>2</sup> s <sup>-1</sup> )	$1.7 \times 10^{-9}$	(Foussard and Debellefontaine, 2000)
$k_{O_3/HO_2^-}$ (m <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup> )	$2.8 \times 10^9 \pm 0.5 \times 10^9$	(Staehelin and Hoigne, 1982)
<b>O<sub>2</sub></b>		
$H_{O_2}$ (Pa m <sup>3</sup> mol <sup>-1</sup> )	$7.3 \times 10^4$	(Roustan, 2003)
$D_{O_2}$ (m <sup>2</sup> s <sup>-1</sup> )	$2.1 \times 10^{-9}$	(Roustan, 2003)
<b>ClOH/ClO<sup>-</sup></b>		
$K_1$ (Cl <sub>2</sub> → HClO)	$\left(\exp\left(\frac{53}{R}\right) \exp\left(-\frac{33000}{RT}\right)\right) + 1.02 \left(\left(\frac{l^{0.5}}{1+l^{0.5}} - \frac{0.5^{0.5}}{1+0.5^{0.5}}\right) + 0.23(0.5-l)\right)$	Eq. deduced from (Wang and Margerum, 1994)
	$\Rightarrow 3.8 \times 10^{-4}$ at $l = 0$ et 293 K	
$pK_{A,1}$ (ClOH/ClO <sup>-</sup> )=	$\frac{3000}{T} - 10.0686 + 0.0253 \times T \Rightarrow 7.58$ at 293K	(Morris, 1967)
$D_{ClO^-}$ (m <sup>2</sup> s <sup>-1</sup> )	$10^{\frac{-1060}{T} - 5.40} \Rightarrow 0.96 \times 10^{-9}$ at 293K	(Chao, 1968)
$D_{ClOH}$ (m <sup>2</sup> s <sup>-1</sup> )	$10^{\frac{-945}{T} - 5.72} \Rightarrow 1.13 \times 10^{-9}$ at 293K	(Chao, 1968)
<b>H<sub>2</sub>O<sub>2</sub>/HO<sub>2</sub><sup>-</sup></b>		
$pK_{A,4}$	11.8	(Beltrán, 2004)

Table A.2: Suppliers and references of the chemical products and equipments used.

Chemical products			
NaOH	10 mol L <sup>-1</sup>	Labogros	France
H <sub>3</sub> PO <sub>4</sub>	85% wt	Acros Organics	Belgium
NaOCl	13% wt	Acros Organics	Belgium
H <sub>2</sub> O <sub>2</sub>	35% wt	Acros Organics	Belgium
Acetic acid	99.9%	Acros Organics	Belgium
Indigo carmine	Analytical grade	Acros Organics	Belgium
Sodium thiosulfate	Titrisol® 0.1 mol L <sup>-1</sup>	Merck	Germany
Potassium iodide	Analytical grade	Acros Organics	Belgium
Ammonium molybdate	98.5 0025	Rectapur VWR	Belgium
O <sub>2</sub> (cylinder)	Pure	Air Liquide	France
N <sub>2</sub> /H <sub>2</sub> S mixture (cylinder)	1000 ± 50 ppmv in H <sub>2</sub> S	Air liquide	France
Equipments			
Float type flowmeters	Brooks Instrument	Sho Rate R6-15-B (liquids)	USA
		Sho Rate R6-15-C (air)	
		Sho Rate R6-15-D (H <sub>2</sub> S/N <sub>2</sub> )	
Float type flowmeter in Teflon®	Gilmont	GF-1360	USA
Centrifugal pumps	Iwaki	Magnet Pump MD-30FX	Japan
Gas membrane pump	KNF	N816.1.2KN.45.18	France
Static mixer	Koflo	3/8 OD	Japan
Bourdon manometers	Bamo	63 P60.5	France
Ozone generator	Trailigaz	24 g h <sup>-1</sup> fed with O <sub>2</sub>	France
Ion chromatograph	Dionex	DX 120	USA
Ozone analyzer	Trailigaz	Uvozon 200	France
Combined pH-T probe	Schott	Blue Line 14 pH	Germany
O <sub>2</sub> probe	WTW	Cellox 325	Germany

Table A. 3: Results of the ozone absorption experiments using the operating conditions of Table 1.

$C_{H_2O_2,i}$ (mg L <sup>-1</sup> )	$C_{H_2O_2,o}$ (mg L <sup>-1</sup> )	$pH$	$Q_L$ (L h <sup>-1</sup> )	$Q_G$ (NL h <sup>-1</sup> )	$U_{SG}$ (m s <sup>-1</sup> )	$Eff_{O_3}$ (%)	$a^\circ$ (m <sup>2</sup> m <sup>-3</sup> )	$Ha$
1173	606	9.9	6.9	482	1.13	21.3	75.1	4.16
1173	538	9.9	6.9	606	1.27	20.8	80.2	3.92
1173	797	9.9	14.0	680	1.34	23.6	76.7	4.78
1173	762	9.9	12.2	762	1.44	21.5	77.7	4.67
1471	1071	10.04	14.0	642	1.18	33.2	76.1	5.93
1471	1197	9.99	21.2	720	1.27	33.6	81.3	6.11
1683	835	10.07	6.9	462	1.18	32.2	77.9	6.93
1683	888	10.07	6.9	496	1.25	28.5	70.0	6.73
1683	1250	10.03	14.0	567	1.36	30.8	71.4	6.91
1683	1262	10	14.0	633	1.44	29.1	72.8	7.56
1794	947	10.15	6.9	500	1.24	33.7	74.7	7.52
1794	1360	10.07	14.0	577	1.34	34.2	71.4	7.58
1794	1375	10.06	14.0	650	1.40	32.8	72.7	7.90
1794	1496	10.03	21.2	754	1.46	33.4	78.3	7.93
2720	1701	10.01	6.9	465	1.18	42.2	85.3	8.29
2720	1792	9.99	6.9	498	1.25	37.8	76.8	8.09
2720	2298	9.92	14.0	594	1.30	34.0	64.8	8.52
2720	2238	9.91	14.0	628	1.45	37.5	85.0	6.49
2720	2425	9.92	21.2	717	1.54	35.1	78.0	6.48